

MgH₂-CARBON COMPOSITES FOR HYDROGEN STORAGE

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Introduction

It is well-known that magnesium and its alloys are promising materials for hydrogen storage due to high capacity of forming hydrides and reversibility of hydrogen sorption/desorption process. However, slow hydrogenation reaction and high temperature of hydrogen release (more than 300°C) put obstacles on the way of magnesium use for hydrogen storage. The present investigation is devoted to the development of magnesium modification methods which should allow improving the kinetics and decreasing the temperature of dehydrogenation.

The most interesting method for improving kinetics of magnesium interaction with hydrogen is mechanochemical activation leading to high concentration of defects and increase of active surface. In the case of magnesium hydride based systems mechanochemical activation results in a appreciable improvement of the hydrogenation rate [1]. The hopeful results have been obtained in [2] where mixture of magnesium with graphite was ball milled. Hydrogenation of such composites has been realized at temperature of less than 200°C and the peak of thermodesorption has been shifted into the area of lower temperatures.

In the present work magnesium hydride as a starting material has been used for higher effectiveness of mechanochemical treatment. Magnesium hydride is less plastic and more fragile material as compared with metallic magnesium [3].

Results and discussion

Hydrogen-storage characteristics of samples of four types were studied: as synthesized MgH₂(1), MgH₂ after mechanochemical activation, m/a (2); MgH₂-graphite (3) and MgH₂-carbon nanofibers (CNF) both after mechanochemical activation.

The process of interaction of magnesium powder with hydrogen under various pressures and temperatures was investigated in details and it was shown that: a) at 450°C the hydrogenation process started rapidly and reached the fractional conversion of 0.80-0.85 in 20-30 minutes, after that the rate of hydrogen absorption slowed down

harshly; b) variation of hydrogenation temperature within the range of 300 to 500°C did not affect the fractional conversion, but influenced only the rate of hydrogen absorption at initial stage of hydrogenation; c) increase in hydrogen pressure from 15 to 55 MPa caused an acceleration of absorption at initial stage of hydrogenation only.

The obtained results have shown that diffusion of hydrogen through the layer of formed hydride is the limit stage of process of magnesium hydrogenation.

In order to evaluate the phase relationships in the MgH₂-graphite system a treatment of the mixtures under high quasihydrostatic pressures (3 GPa, 800°C, 1 h.) has been done. As a result, formation of magnesium carbide nor graphite intercalation compounds were not detected. High pressure modification γ -MgH₂ has been found in the system treated. Besides that, preliminary mechanochemical treatment promoted the formation of this metastable high pressure modification.

It has been shown that mechanochemical treatment led to substantial increase of specific surface of composites obtained in comparison with initial magnesium hydride and graphite (Table 1).

Table 1. specific surface of initial materials and composites obtained.

Composition	specific surface, m ² /g
Mg	0.1
MgH ₂	1.7
graphite	7
MgH ₂ m/a	6.2
MgH ₂ :graphite (1:1) m/a	63

Fig. 1 shows the results obtained under thermal decomposition of samples using the method of prolong exposure at constant temperature. As one can see, the pressure of hydrogen release from the samples at 150 and 250°C is higher after the mechanochemical treatment as compared with non-treated powder MgH₂. This effect is much more pronounced for the samples with graphite.

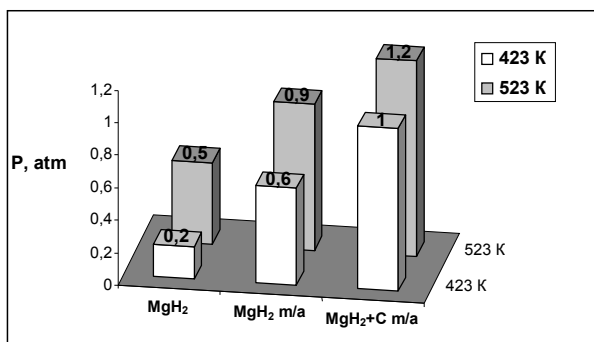


Fig. 1. Desorption pressures at 150 and 250 C for the samples studied.

Hydrogenation of mechanochemically treated samples with graphite after the thermal decomposition led to the increase of the hydrogen sorption rate in comparison with magnesium produced during thermal decomposition of non-treated MgH₂.

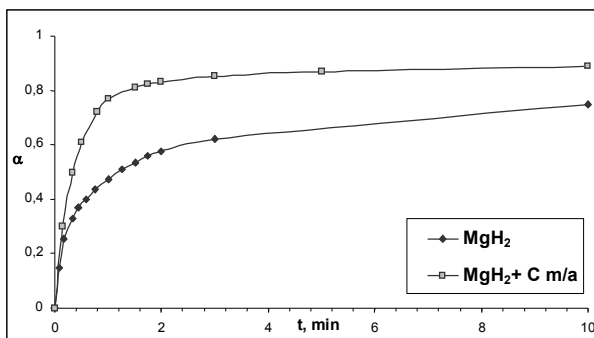


Fig. 2. The fractional conversion (α) of magnesium hydrogenation reaction at 330°C for samples after thermal decomposition

CNFs have been used as another carbon component for obtaining MgH₂-C composites. The degree of amorphisation of composites obtained was substantially higher as compared with the MgH₂-graphite composites. This is likely concerned

the difference in the carbon component nature and their behaviour during the treatment. The pressures of hydrogen release from such composites at the temperatures of 150 and 250°C were also higher than the desorption pressures of non-treated MgH₂.

Conclusions

Peculiarities of hydrogenation reactions of magnesium at temperatures of 410°C to 450°C and pressures of 15 to 55 MPa have been investigated.

Interactions in MgH₂-graphite system under quasihydrostatic conditions (3 GPa, 800°C, 1 h.) have been explored. It has been shown that such a treatment did not lead to formation of new chemical compounds. The phase transformation of MgH₂ to a metastable high-pressure modification has been found.

As a result of mechanochemical activation, the MgH₂-graphite and MgH₂-CNF composites have been obtained. It has been pointed that the mechanochemical treatment of mixtures of magnesium hydride with carbon affect strongly the kinetic parameters of hydrogen desorption but also led to decreasing of the thermal stability of the hydride phase.

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References

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